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NITROGUANIDINE WASTEWATER POLLUTION CONTROL TECHNOLOGY: PHASE II
WASTEWATER CHARACTERIZATION AND ANALYTICAL METHODS
DEVELOPMENT FOR ORGANICS

ELIZABETH P. BURROWS, Ph.D.
ERNST E. BRUEGEMANN
STEVEN H. HOKE, Ph.D.
EVELYN H. MCNAMEE
LOUANNA J. BAXTER

PREPARED FOR
US ARMY TOXIC AND HAZARDOUS MATERIALS AGENCY
ABERDEEN PROVING GROUND, MD 21010

U S ARMY MEDICAL BIOENGINEERING RESEARCH & DEVELOPMENT LABORATORY

Fort Detrick

Frederick, Maryland 21701

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PREFACE

The research reported herein was performed at the request of the US Army Toxic and Hazardous Materials Agency (USATHAMA), Aberdeen Proving Ground, MD, under R&D Project No. 1L162720D048, "Nitroguanidine Wastewater Pollution Control Technology Development," Mr. Charles Denzler, Project Engineer. This study is part of the DARCOM Pollution Abatement and Environmental Control Technology Program conducted by USATHAMA.

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INTRODUCTION AND OBJECTIVES

Review of several documents¹⁻⁴ indicates that nitroguanidine production wastewater may contain, in addition to nitroguanidine and inorganic ions, nitrosoguanidine, cyanoguanidine, guanidine, urea, cyanamide, melamine, and ammeline. Our objective was to develop optimal methodology for each compound individually and then to apply the methodology to wastewaters from Sunflower Army Ammunition Plant (SFAAP).

MATERIALS AND METHODS

CHEMICALS

Nitroguanidine (NQ) was purchased (Aldrich Chemical Co.) and purified by recrystallization from water. Nitrosoguanidine (NSQ) was synthesized by zinc dust treatment of NQ according to the published procedure.⁵ Cyanoguanidine (CNQ, Eastman Kodak), guanidine hydrochloride (Aldrich), cyanamide (Fisher), melamine (Chemical Service Co.), ammeline (Pfaltz & Bauer), *m*-phenylenediamine dihydrochloride (Fisher), and sodium pentacyanoammine ferrate (SPF, Fisher) were commercial products used without further purification. The diagnostic test kit used for urea determinations, No. 640, was purchased from Sigma.

HIGH PRESSURE LIQUID CHROMATOGRAPHIC (HPLC) ANALYSES

A Waters liquid chromatographic system (Waters Associates, Milford, MA) consisted of the following components: two Model 6000A solvent delivery systems, a Model 721 programmable systems controller, a Model 730 data module, a Lamda-max Model 480 LC spectrophotometer, and a Model 710B Waters intelligent sample processor (WISP). A Zorbax C₈ reverse phase stainless steel column (25 cm x 4.6 mm ID, particle size 6 μ m, DuPont Instruments, Wilmington, DE) was used.

Conditions for NQ, NSQ, and CNQ were as follows: mobile phase, glass-distilled deionized water; flow rate, 0.8 mL/min. Effluent was monitored at 235 nm, 0.05 absorbance units full scale (AUFS). Injection volume was 20 μ L. Standard solutions of concentrations 10, 5, 2, 1, and 0.5 mg/L were prepared by dilution of a stock solution freshly prepared each day of analysis.

Conditions for melamine and ammeline were as follows: mobile phase, 28% methanol in 0.005 M octanesulfonic acid adjusted to pH 3 with acetic acid; flow rate 1.5 mL/min. Effluent was monitored at 235 nm, 0.1 AUFS, and injection volume was 200 μ L. Standard solutions of concentrations 4, 2, 1, 0.4, and 0.2 mg/L were prepared as above.

Precision and accuracy data for the HPLC analyses are given in Appendix A. Correlation coefficients (r^2) were >0.9995.

ION CHROMATOGRAPHIC ANALYSES

A Dionex Model 16 ion chromatograph, interfaced with a Varian Vista 401 data station and equipped with a Dionex #30831 cation exchange column in conjunction with a cation concentrator pre-column (Dionex #30830), was used to determine guanidine. Eluent was 0.25 mM *m*-phenylenediamine dihydrochloride in 0.25 mM hydrochloric acid at a flow rate of 2.5 mL/min. The hollow fiber suppressor (Dionex #035352, see Results and Discussion) was regenerated with 0.04 M potassium hydroxide at a flow rate of 2 to 3 mL/min. Samples were injected manually via a 3-mL plastic Luer-Lok syringe into a 100 μ L sample loop. The instrument was calibrated by injection of 50, 25, 10, 5, and 1 mg/L standard solutions, prepared from guanidine hydrochloride in water. Response was linear over this range with a typical correlation coefficient of 0.999, and the detection limit (signal to noise ratio 2) was <0.5 mg/L. Replicate analyses of samples containing 1, 10, and 40 mg/L are summarized in Table 1.

TABLE 1. PRECISION AND RECOVERY IN GUANIDINE DETERMINATION BY ION CHROMATOGRAPHY

Replicate No.	Concentration (mg/L)			Low Spike ^a	Medium Spike ^a
	Low	Medium	High		
1	0.99	10.1	41.0	8.79	41.9
2	0.90	10.4	40.8	8.89	43.2
3	0.91	10.9	40.7	8.84	43.2
4	0.96	9.8	40.4	9.00	42.8
5	0.97	10.4	40.8	9.08	42.9
6	0.94	10.2	41.0	8.87	42.5
7	0.94	10.3	39.7	8.89	43.0
Mean	0.94	10.3	40.6	8.91	42.8
Std. Deviation	±0.03	±0.34	±0.46	±0.10	±0.46
Rel. Std. Deviation	3.4%	3.3%	1.1%	1.1%	1.1%
% Recovery ^a				97%	99%

a. Calculations for concentrations of spiked samples and percent recoveries are given in Appendix B.

SPECTROPHOTOMETRIC ANALYSES

A Beckman 5230 UV/visible spectrophotometer was used for colorimetric determinations of urea and cyanamide. Urea was hydrolyzed by urease and determined by measurement of the absorbance of indophenol at 570 nm. The procedure recommended by Sigma⁶ was followed. Cyanamide was determined by measurement of absorbance of the pentacyanoamine ferrate complex at 530 nm.^{7,8} Six standard solutions of concentrations over the range 6 to 0.1 mg/L were freshly prepared each day of analysis by dilution of a stock solution of 0.1 M

cyanamide (4.205 g/L). The stock solution was prepared once a week and kept refrigerated. SPF solution (0.02 M) was freshly prepared daily. Three 2-mL replicates of each standard solution were added to test tubes containing 0.2 M pH 10.5 sodium carbonate buffer⁷ (1 mL) and SPF solution (1 mL). The mixtures were shaken thoroughly and allowed to stand 45 min before absorbance readings at 530 nm were taken. Reagent blanks were subtracted from the readings. Precision and recovery data are listed in Appendix C; correlation coefficients were 0.9999.

THIN LAYER CHROMATOGRAPHIC (TLC) ANALYSES

Cellulose plates were used and were developed in the following systems: 3N NH₄OH/methanol (60:75, system 1), n-butanol/ethanol/water (4:1:1, system 2), and 2-propanol/conc NH₄OH/water (8:1:1, system 3). Samples were applied to the plates from methanol solutions, except in the case of ammeline, which was very sparingly soluble in water and hydroxylic solvents and was applied from 5N formic acid solution. In most cases optimum visualization of the spots was achieved by dipping in 3N NH₄OH/0.1N AgNO₃ (1:1) followed by air-drying and heating 10 min at 100°. CNQ and cyanamide were detected by ferricyanide/nitroprusside spray reagent⁹ (FCNP) and urea by p-dimethylamino-benzaldehyde/1N HCl⁹ (DAB) spray.

RESULTS AND DISCUSSION

HPLC proved to be the method of choice for all ultraviolet-absorbing compounds, which include NQ, NSQ, CNQ, melamine, and ammeline. Wastewater samples could conveniently be injected onto the column without extraction or pretreatment. Detection limits and retention times are summarized in Table 2. Sensitivity for NQ at 235 nm was found comparable to that reported previously at 263 nm,^{3,10} while sensitivity for NSQ at 235 nm was tenfold greater. The use of water as mobile phase afforded better resolution and more efficient yet rapid separation of the substituted guanidines.

TABLE 2. HPLC ANALYSES OF POSSIBLE NITROGUANIDINE WASTEWATER CONSTITUENTS

Compound	Low Standard (mg/L)	Injection Volume (μL)	Detection Limit ^a (μg/L)	Retention Time (min)
Nitroguanidine	0.50	20	100	6.0
Nitrosoguanidine	0.50	20	42	4.6
Cyanoguanidine	0.51	20	170	5.4
Melamine	0.21	200	28	10.1
Ammeline	0.20	200	21	9.2

a. Signal to noise ratio 2.

Typical injections of standards for NQ, NSQ, and CNQ, and for ammeline and melamine are depicted in Figures 1 and 2, respectively. Figure 3 illustrates a typical HPLC analysis of NQ process wastewater in which ammeline at 0.38 mg/L and melamine at 0.23 mg/L were detected in tank 105 before treatment at SFAAP. After treatment, 0.089 mg/L ammeline remained, and melamine was below detection limit. For analyses of these and other SFAAP wastewater samples for other constituents, see Methods Application section.

Guanidine, not amenable to HPLC detection, was optimally determined conductimetrically as the cation by ion chromatography. The method necessitates utilization of a suppressor to reduce the background conductivity of the eluent which in turn enhances the conductivity signal of the analyte. During initial attempts using a suppressor resin, successive sample injections resulted in increasingly longer retention times. This problem, attributed to possible interaction of guanidinium ion or nitroguanidine with the suppressor resin, was eliminated by replacing the suppressor resin with a fiber suppressor. With this system, anions are exchanged through a membrane wall, thus minimizing any undesirable interactions.

Under the previously described conditions, the retention time of guanidinium ion is 5.1 min. Common monovalent cations, e.g., Na^+ , K^+ , and NH_4^+ , have shorter retention times (1.6 to 2.0 min) and do not interfere. Divalent cations, e.g., Ca^{++} and Mg^{++} , elute in excess of 30 min. In summary, the method appears to be highly reproducible, with few interferences and adequate sensitivity. It should be noted, however, that during development of the method the cation column began to turn pink. This was attributed to slow polymerization of m-phenylenediamine and attachment of the polymer to the resin. There was no immediate effect on the separations, and it was found that polymerization was minimal if air was excluded from eluent reservoirs and columns were covered with aluminum foil to exclude light. Under these conditions, cation columns should last 6 months or longer.

Cyanamide also could not be analyzed by HPLC, but was determined spectrophotometrically by complexation with pentacyanoammine ferrate reagent.⁷ The method is specific for cyanamide and was not subject to interferences by other organic constituents of NQ production wastewater. Detection limits were below 0.1 mg/L unless high concentrations of inorganic salts were present.

TLC separations of the expected NQ wastewater constituents were also investigated, and optimum parameters are summarized in Table 3. Several disadvantages are readily apparent. Detection limits are frequently greater by several powers of ten relative to HPLC, and the spots, visualized by chromogenic spray or dip reagents (see Table 3), cannot be readily quantitated. Furthermore, interferences from dissolved inorganic salts in wastewaters preclude direct application of aqueous solutions to the plates, and the organic constituents are generally too polar for efficient extraction by organic solvents.

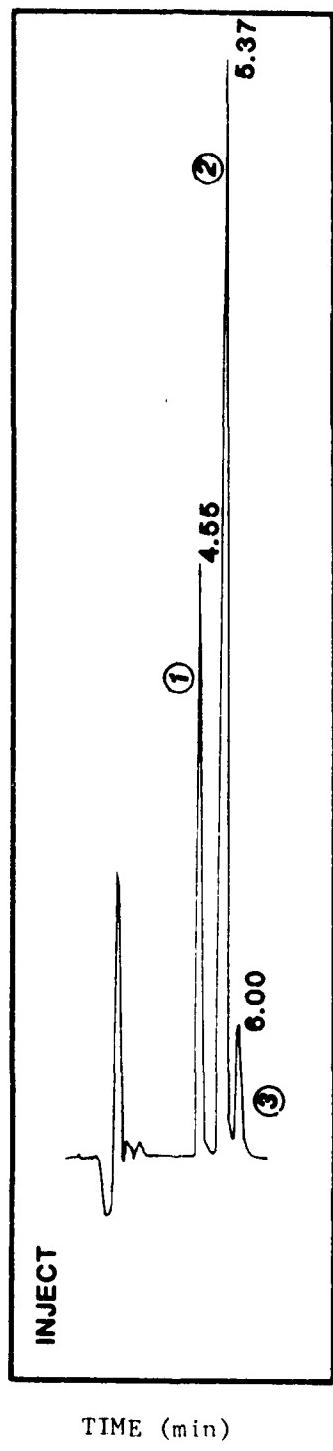
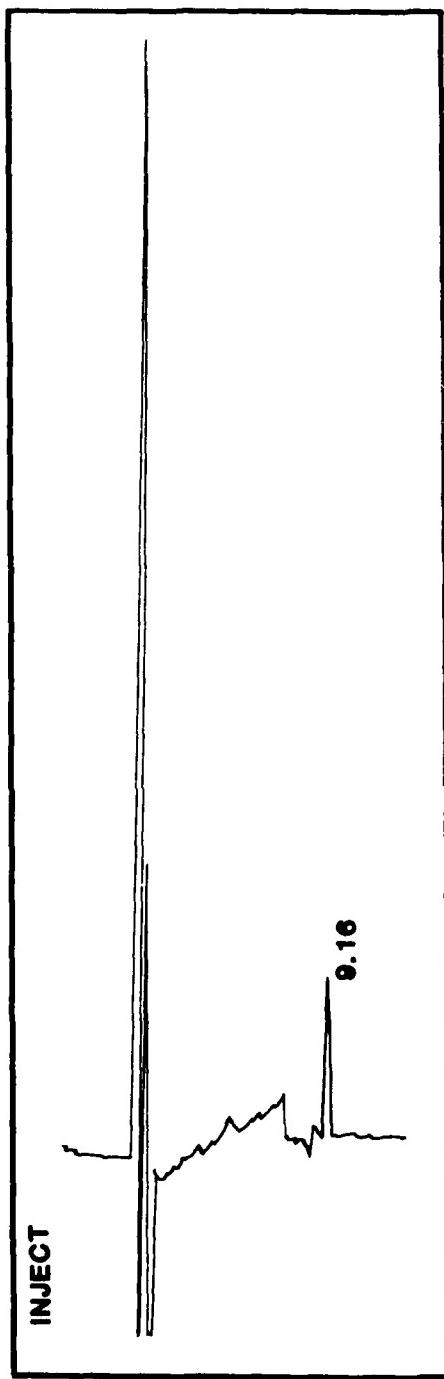
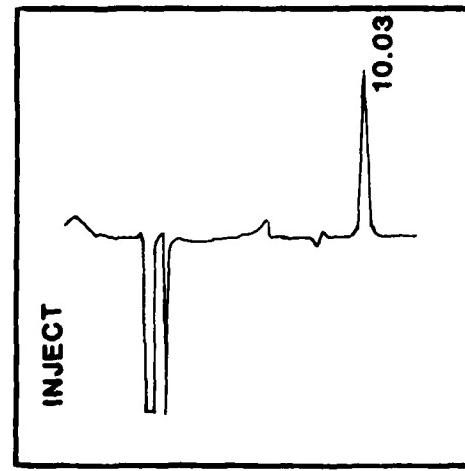


Figure 1. HPLC standards: nitrosoguanidine (1, 1.72 mg/L), cyanoguanidine (2, 5.09 mg/L), nitroguanidine (3, 0.33 mg/L).



(a)



(b)

TIME (min)

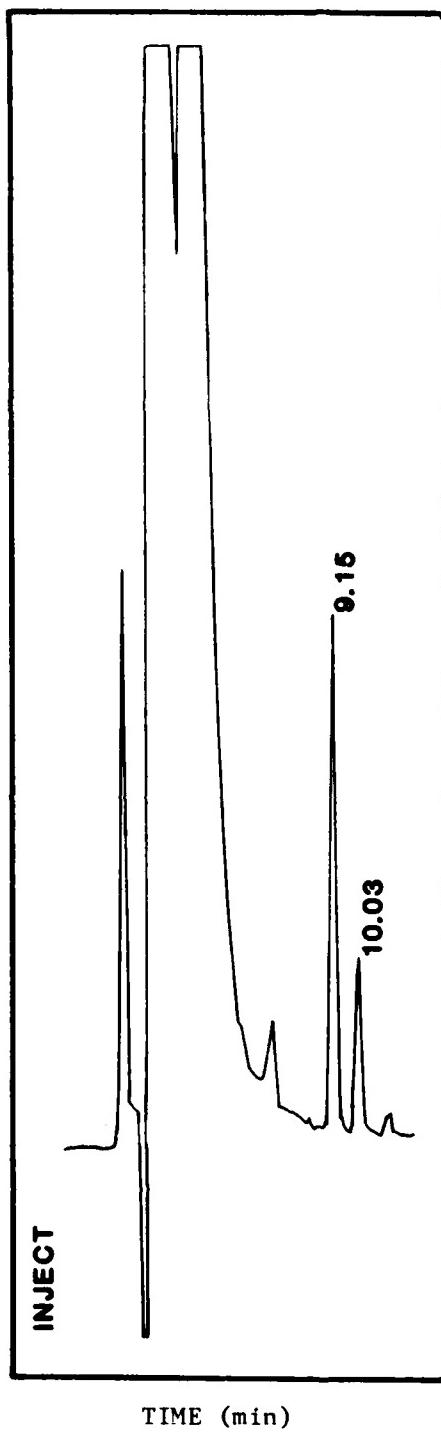


Figure 3. HPLC analysis of tank 105, Sunflower Army Ammunition Plant, before treatment.

TABLE 3. TLC PARAMETERS FOR POSSIBLE NITROGUANIDINE WASTEWATER CONSTITUENTS

Compound	Optimum Solvent System	Chromogenic Reagent	Color	R _F	Detection (μg)
Guanidine	1	AgNO ₃ /NH ₄ OH	Brown/Brown	0.8	2
Cyanoguanidine	2	FCNP	Pink-purple	0.45	1
Melamine	2	AgNO ₃ /NH ₄ OH	White/Brown	0.25	0.5
Ammeline	2	AgNO ₃ /NH ₄ OH	Brown/Brown	0.45	5
Cyanamide	2	FCNP	Pink-purple	0.8	0.2
Urea	3	DAB	Yellow	0.6	1

METHODS APPLICATION

While methods development was at an early stage (November 1982), water samples were taken from certain SFAAP locations for analysis. Because the samples were stored (under refrigeration) for at least several months prior to analysis of trace organics, those results (Table 4) may be considered as only indicative of the original content. Table 5 summarizes recent analyses (October 1983) of wastewater from Tank 105, before and after treatment with lime/steam. The sample after treatment was, at our request, neutralized with HCl to prevent possible further reaction on standing. Because dimerization of cyanamide to CNQ is rapid at pH >7, and very little of the latter was detected, cyanamide was not sought.

TABLE 4. ANALYSES OF SFAAP WATER^a

Analyte (mg/L)	Trailer (9.6)	Location (pH)			Wet NQ Sump (8.8)
		NQ	SE	Sump (11.3)	
NQ	2		327		915
CNQ	ND		ND		<0.17
NSQ	ND		ND		0.43
Ammeline	ND		ND		<0.021
Melamine	ND		ND		0.060
Guanidine	85		85	63	ND
TKN	700		1,150	125	330
NH ₃ -N	140		235	75	ND
C1 ⁻	30		30	20	180
NO ₂ ⁻	360		745	7	5
NO ₃ ⁻	14		13	845	110
SO ₄ ⁼	190		215	59	1,690

a. ND - not determined.

TABLE 5. ANALYSIS OF WASTEWATER FROM
SFAAP TANK 105 (mg/L)

Analyte	Before Treatment (pH 8.2)	After Treatment ^a (pH 6.9)
NQ	2849	0.54
CNQ	<0.17	<0.17
NSQ	<0.042	<0.042
Ammeline	0.377	0.089
Melamine	0.230	<0.028
Guanidine ^b	-	10.8 ^c
Urea	<15	1,240 ^c
TKN	659	985
NH ₃ -N	5.5	40.5
Cl ⁻	130	>400 ^d
NO ₂ ⁻	20	840 ^c
NO ₃ ⁻	1.8	1.6
SO ₄ ⁼	98	80

a. Neutralized, not corrected for dilution.

b. Not possible to determine in presence of very large excess of NQ.

c. Formed from NQ by treatment.

d. From HCl added to neutralize sample.

REFERENCES

1. Letter, HSHB-EW/WP, 25 June 1982, subject: Water Quality Consultation No. 32-24-0364-82, Sunflower Army Ammunition Plant, DeSota, KS, 1-5 February 1982.
2. American Cyanamid Co. 1955. Studies Relating to Effluent Disposal in Nitroguanidine Manufacture. Toxicity of Welland Effluent to Stream Life and to Animals, and Treatment Proposed to Eliminate Toxic Effects of Such Effluent. American Cyanamid Co., Stamford, CT. Contract No. DAI-30-069-501-ORD-(P)-1220.
3. Kaplan, D.L., J.H. Cornell, and A.M. Kaplan. 1981. Microbiological and Chemical Transformations of Nitroguanidine. Technical Report 81/019. US Army Natick Research and Development Laboratories, Natick, MA.
4. Kenyon, K. 1982. A Data Base Assessment of Environmental Fate Aspects of Nitroguanidine. Technical Report 8214. US Army Medical Bioengineering Research and Development Laboratory, Fort Detrick, Frederick, MD.
5. Davis, T.L. and E.N. Rosenquist. 1937. Studies in the Urea Series. XV. Transformations of Nitrosoguanidine. J. Am. Chem. Soc. 59(15):2112-2115.
6. Sigma Chemical Co. 1974. The Colorimetric Determination of Urea Nitrogen. Sigma Technical Bulletin No. 640. St. Louis, MO.
7. Buyske, D.A. and V. Downing. 1960. Spectrophotometric Determination of Cyanamide. Anal. Chem. 32(13):1798-1800.
8. Neiman, T.A., F.J. Holler, and C.G. Enke. 1976. Reaction Rate Method for Determining Trace Concentrations of Cyanamide. Anal. Chem. 48(6):899-902.
9. Stahl, E., ed. 1969. Thin Layer Chromatography. 2nd Edition, pp. 869,891. Springer-Verlag, Berlin.
10. Kaplan, D.L., J.H. Cornell, and A.M. Kaplan. 1982. Decomposition of Nitroguanidine. Environ. Sci. Technol. 16(8):488-492.

APPENDIX A

PRECISION AND ACCURACY OF HPLC ANALYSES OF NQ, NSQ, CNQ, MELAMINE, AND AMMELINE

PRECISION

Precision of the method was determined by injecting a sample four times on three separate days. Mean, standard deviation, and relative standard deviation were calculated for a low and high concentration.

1. Nitroguanidine

<u>Day</u>	<u>Date</u>	<u>Mean (mg/L)</u>	<u>Standard Deviation (±)</u>	<u>Relative Standard Deviation (%)</u>
<u>Low Concentration</u>				
1	7 July 83	0.220	0.010	4.54
2	13 July 83	0.220	0.004	1.82
3	14 July 83	0.220	0.010	4.54
	<u>Overall</u>	<u>0.220</u>	<u>0.008</u>	<u>3.63</u>
<u>High Concentration</u>				
1	7 July 83	5.05	0.03	0.59
2	13 July 83	5.03	0.02	0.40
3	14 July 83	5.03	0.03	0.60
	<u>Overall</u>	<u>5.04</u>	<u>0.03</u>	<u>0.53</u>

2. Nitrosoguanidine

<u>Day</u>	<u>Date</u>	<u>Mean (mg/L)</u>	<u>Standard Deviation (±)</u>	<u>Relative Standard Deviation (%)</u>
<u>Low Concentration</u>				
1	1 Aug 83	0.50	0.01	2.00
2	2 Aug 83	0.50	0.02	4.00
3	4 Aug 83	0.49	0.01	2.04
	<u>Overall</u>	<u>0.50</u>	<u>0.01</u>	<u>2.68</u>
<u>High Concentration</u>				
1	1 Aug 83	10.22	0.06	0.59
2	2 Aug 83	10.33	0.07	0.68
3	4 Aug 83	10.02	0.06	0.60
	<u>Overall</u>	<u>10.19</u>	<u>0.06</u>	<u>0.62</u>

3. Cyanoguanidine

<u>Day</u>	<u>Date</u>	<u>Mean (mg/L)</u>	<u>Standard Deviation (±)</u>	<u>Relative Standard Deviation (%)</u>
<u>Low Concentration</u>				
1	25 July 83	0.49	0.01	2.04
2	26 July 83	0.48	0.01	2.08
3	27 July 83	0.49	0.02	4.08
	<u>Overall</u>	<u>0.49</u>	<u>0.01</u>	<u>2.73</u>
<u>High Concentration</u>				
1	25 July 83	10.23	0.08	0.78
2	26 July 83	10.15	0.02	0.20
3	27 July 83	10.38	0.02	0.19
	<u>Overall</u>	<u>10.25</u>	<u>0.04</u>	<u>0.39</u>

4. Melamine

<u>Day</u>	<u>Date</u>	<u>Mean (mg/L)</u>	<u>Standard Deviation (±)</u>	<u>Relative Standard Deviation (%)</u>
<u>Low Concentration</u>				
1	24 May 83	0.21	0.01	4.76
2	25 May 83	0.21	0.01	4.76
3	26 May 83	0.21	0.01	4.76
	<u>Overall</u>	<u>0.21</u>	<u>0.01</u>	<u>4.76</u>
<u>High Concentration</u>				
1	24 May 83	2.10	0.01	0.48
2	25 May 83	2.10	0.01	0.48
3	26 May 83	2.09	0.01	0.48
	<u>Overall</u>	<u>2.10</u>	<u>0.01</u>	<u>0.48</u>

5. Ammeline

<u>Day</u>	<u>Date</u>	<u>Mean (mg/L)</u>	<u>Standard Deviation (±)</u>	<u>Relative Standard Deviation (%)</u>
<u>Low Concentration</u>				
1	31 May 83	0.19	0.01	5.26
2	01 June 83	0.18	0.01	5.56
3	02 June 83	0.19	0.01	5.26
	<u>Overall</u>	<u>0.19</u>	<u>0.01</u>	<u>5.36</u>
<u>High Concentration</u>				
1	31 May 83	2.06	0.01	0.40
2	01 June 83	2.04	0.02	0.98
3	02 June 83	2.03	0.02	0.99
	<u>Overall</u>	<u>2.04</u>	<u>0.02</u>	<u>0.82</u>

ACCURACY

Accuracy is better defined as percent recovery. This is determined by taking an aliquot of a sample of low concentration and adding a spike to double the concentration. The aliquot is then analyzed four times to obtain a mean, standard deviation, relative standard deviation and percent recovery. This is repeated for a sample of high concentration.

1. Nitroguanidine

<u>Day</u>	<u>Mean (mg/L)</u>	<u>Standard Deviation (±)</u>	<u>Relative Standard Deviation (%)</u>	<u>% Accuracy</u>
<u>Low Level</u>				
1	1.53	0.01	0.65	104.79
2	1.51	0.01	0.66	100.00
3	1.54	0.01	0.65	96.86
				<u>100.55</u>
<u>High Level</u>				
1	7.46	0.01	0.13	101.08
2	7.34	0.02	0.27	100.96
3	7.34	0.05	0.68	100.96
				<u>101.00</u>

2. Nitrosoguanidine

<u>Day</u>	<u>Mean (mg/L)</u>	<u>Standard Deviation (±)</u>	<u>Relative Standard Deviation (%)</u>	<u>% Accuracy</u>
<u>Low Level</u>				
1	1.61	0.01	0.62	101.90
2	1.70	0.05	2.94	98.27
3	1.54	0.05	4.55	<u>100.65</u> <u>100.27</u>
<u>High Level</u>				
1	7.44	0.04	0.54	100.54
2	7.45	0.04	0.54	99.33
3	7.18	0.05	0.70	<u>98.49</u> <u>99.45</u>

3. Cyanoguanidine

<u>Day</u>	<u>Mean (mg/L)</u>	<u>Standard Deviation (±)</u>	<u>Relative Standard Deviation (%)</u>	<u>% Accuracy</u>
<u>Low Level</u>				
1	1.51	0.01	0.66	100.67
2	1.50	0.02	1.33	100.00
3	1.65	0.02	1.21	<u>102.48</u> <u>101.05</u>
<u>High Level</u>				
1	7.55	0.02	0.26	100.94
2	7.39	0.03	0.41	100.14
3	7.66	0.06	0.78	<u>102.00</u> <u>101.03</u>

4. Melamine

<u>Day</u>	<u>Mean (mg/L)</u>	<u>Standard Deviation (±)</u>	<u>Relative Standard Deviation (%)</u>	<u>% Accuracy</u>
<u>Low Level</u>				
1	0.62	0.01	1.61	101.64
2	0.61	0.01	1.64	100.00
3	0.61	0.01	1.64	100.00
				<u>100.55</u>
<u>Medium Level</u>				
1	2.97	0.01	0.34	100.34
2	2.96	0.01	0.34	100.00
3	2.93	0.01	0.34	98.99
				<u>95.03</u>

5. Ammeline

<u>Day</u>	<u>Mean (mg/L)</u>	<u>Standard Deviation (±)</u>	<u>Relative Standard Deviation (%)</u>	<u>% Accuracy</u>
<u>Low Level</u>				
1	0.59	0.01	1.69	101.72
2	0.59	0.01	1.69	101.72
3	0.59	0.01	3.34	101.72
				<u>101.72</u>
<u>Medium Level</u>				
1	2.88	0.01	0.35	100.77
2	2.87	0.02	0.70	101.41
3	2.88	0.02	0.69	101.77
				<u>101.65</u>

APPENDIX B

CONCENTRATIONS OF SPIKED GUANIDINE SAMPLES

1. Low spike:

$$1 \text{ mL of } 0.94 \text{ mg/L} + 10 \text{ mL of } 10 \text{ mg/L} = 9.18 \text{ mg/L}$$

2. Medium spike:

$$2 \text{ mL of } 10.3 \text{ mg/L} + 10 \text{ mL of } 50 \text{ mg/L} = 43.4 \text{ mg/L}$$

PERCENT RECOVERIES OF SPIKED GUANIDINE SAMPLES

1. Low spike:

$$8.91/9.18 \times 100 = 97\%$$

2. Medium spike:

$$42.8/43.4 \times 100 = 99\%$$

APPENDIX C

PRECISION AND RECOVERY IN SPECTROPHOTOMETRIC ANALYSIS OF CYANAMIDE

PRECISION

Precision of the method was determined by analysis of three replicates each of low and high concentration samples on three separate days.

<u>Day</u>	<u>Date</u>	<u>Mean (mg/L)</u>	<u>Standard Deviation</u> <u>±</u>	<u>Relative Standard Deviation %</u>
<u>Low Concentration</u>				
1	16 Jan 84	0.332	0.000	0.00
2	19 Jan 84	0.330	0.014	4.32
3	20 Jan 84	0.330	0.000	0.00
	<u>Overall</u>	<u>0.331</u>	<u>0.005</u>	<u>1.44</u>
<u>High Concentration</u>				
1	16 Jan 84	5.22	0.027	0.52
2	19 Jan 84	5.27	0.024	0.45
3	20 Jan 84	5.24	0.016	0.31
	<u>Overall</u>	<u>5.25</u>	<u>0.022</u>	<u>0.43</u>

RECOVERY

Recovery was determined by analysis of three replicates each of low and high concentration samples spiked to double the concentrations.

<u>Day</u>	<u>Mean (mg/L)</u>	<u>Standard Deviation</u> <u>±</u>	<u>Relative Standard Deviation %</u>	<u>% Accuracy</u>
<u>Low Level</u>				
1	0.361	0.000	0.00	103.38
2	0.350	0.014	3.96	100.53
3	0.351	0.016	4.68	100.57
				<u>101.49</u>
<u>High Level</u>				
1	2.02	0.041	2.00	102.32
2	2.01	0.027	1.36	101.96
3	2.03	0.027	1.31	103.53
				<u>102.60</u>

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